KINETICS AND MECHANISM OF THERMAL DeNOx: A REVIEW

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In 1972 the author, then with Exxon Research and Eng. Co.
(ERE), discovered a new chemical reaction, the gas phase homogeneous
reduction of NO to N2 and H2O by NH3, in the presence of O2 (1,2,3).
This reaction was both rapid and highly selective, i.e. with reaction
times of 0.1 sec or less NO could be nearly quantitatively reduced by
equimolar amounts of NH3 in the presence of O2 concentrations orders
of magnitude greater than the NO. The discovery of this reaction made
possible a new and remarkably simple method of controlling the
emissions of NOx from stationary sources such as utility boilers and
industrial process furnaces, the Thermal DeNOx process. One simply
found the location in the unit at which the temperature was
appropriate to the reaction and installed there a grid to inject NH3
into the hot flue gas.   To date this process has had upwards of 60
commercial applications and in recent instances NO reductions in
excess of 90% have been achieved.

One factor which helped make this success possible was the
development of a predictive kinetic model, i.e. a model which
described the kinetics of the reaction in terms of elementary reaction
rate constants and which could be used to accurately predict the
performance of the process in any given practical application. The
model is routinely used in the engineering design of new Thermal DeNOx
installation.   To the author's knowledge this is the first instance in
which a model based on elementary reaction rate constants has been so
used.   This success was the culmination of the efforts of workers both
within and outside of ERE but this success has recieved less attention
than it might have otherwise.   Several papers and meeting
presentations have outlined the general nature of the model
(4,5,6,7,8), but the actual model itself has been disclosed only in
one somewhat obscure patent (9).   In this review the DDHL model will
be discussed and compaared with models published by others.

The other models of interest were developed by Hanson and
Salimian with subsequent refinement by Hanson and Kimball-Linne
(10,11), by Miller, Branch and Kee (12), and by Silver, Gozewski and
Kolb (13), hereinafter the H&K, MBK, and SGK models, respectively.
Silver and Kolb (14) also measured the rate constant of the NH2 + NO
reaction at elevated temperatures.   Miller et al. are to be credited
with proposing on purely theoretical grounds that the second channel
of the NH2 + NO reaction does not directly yield N2 + H + OH but
rather N2H + OH, a suggestion later supported experimentally by
Andresen et al. (15).   It is to be noted that both of these
contributions were incorporated into the DDHL model.

A principal difference among these modeling efforts was the extent to which experimental data on the kinetics of the NO - NH3 - O2 reaction were available to the modelers. The MBK and SGK models are a prior models, i.e. in the development of these models if the rate constant of a reaction was unknown, it was estimated on purely theoretical grounds without any effort to choose a value that would make the model fit the data. Both these models were successful in qualitative terms in that they showed the appropriate trends when compared to the limited data of Muzio et al. (16). In the H&K model, however, the model seeks to provide a truly quantitative description of the reaction kinetics. Hanson and Kimball-Linne set up a laboratory scale combustor and generated a block of data showing the kinetics of the Thermal DeNOx process for initial temperatures ranging from 1258 K to 1548 K and initial [NO] and [NH3] ranging from 141 to 387 ppm and 78 to 556 ppm, respectively. Since the combustor was operated at a constant air/fuel equivalence ratio of 0.9, neither [O2] nor [H2O] were varied. Sensitivity analysis was done on the model and the rate constants of reactions which were uncertain and sensitive were adjusted to fit the data. Figure 1 shows an example of the model's fit to the data.

The DDHL model was developed in a similar manner, i.e. flow tube experiments were done with synthetic gas mixtures to develop two data bases, one relating to the oxidation of NH3 in the initial absence of NO (T = 1279 to 1323 K, [NH3] = 900 ppm, [O2] = 2 to 8% and [H2O] = 0 or 1%) and the second larger data base relating to the reduction of NO by NH3 (T = 1120 to 1390 K, [O2] = 2 to 8%, [H2O] = 0 to 15%, [NO] = 100 to 460 ppm, [NH3] = 270 to 530 ppm, a total of 742 data points). A kinetic model was developed which gave excellent fit to the former data base and with minor modifications which didn't damage the fit to the NH3 oxidation data base it proved possible to fit the NO reduction data base within 7%, which is within the experimental uncertainty. Figure 2 shows examples of this model's fit to laboratory data (5) while Figure 3 shows a comparison between the model's predicted performance for the Thermal DeNOx process in commercial application and what was obtained.(9)

Since then the DDHL and HSK models were derived in general similar manners, the comparison between them is particularly interesting. While the DDHL model uses 31 elementary reactions of H/N/O species, the H&K model uses 52. Of these 30 reactions are common to the two models, DDHL includes one radical radical reaction which is probably unimportant under Thermal DeNOx conditions and which the H&K model omits. The H&K model includes ten such radical radical reactions. The other reactions which are used in H&K and omitted in DDHL includes three reactions which form nitrogen atoms and four reactions of N2O. The former have high activation energies and will be important only at temperatures well above the Thermal DeNOx range. Since Thermal DeNOx does not make significant amounts of N2O, the latter will be unimportant in the initial absence of N2O. While the DDHL model show the interaction of NH2 and NO as a two channel reaction, capable of yielding N2H + OH and N2 + H2O, the H&K model shows it as having a third far less probable channel yielding HNO + NH. DDHL shows the reactions of NH2 + O, NH + O2, and

NO + HO2 as single channel processes, each making only one pair of
products. While the H&K model agrees that these are the dominant
raction pathways, it does includes a second less important channel for
each. The H&K model also includes the reaction N2H+O2=N2+HO2 with a
rate constant that is 1000 times less at 1200 K than the rate constant
which H&K assumes for the competing N2H+NO=N2+HNO reaction. Thus the
omission of this reaction by DDHL does not appear to be a serious
disagreement.

        Indeed there does not seem to be any disagreement between
the two models as to which reactions are central to the Thermal DeNOx
chemistry. There is also much agreement as to the roles which these
reactions play in deciding the overall kinetics of the Thermal DeNOx
reaction. In both models the overall reaction mechanism may be
divided into two submechanisms, a chain reaction in which NH3 reduces
NO and a chain reaction in which NH3 is oxidized to form NO. In both
submechanisms the first step is the attack on NH3 by O and OH to form
NH2. In the reduction submechanism the NH2 reacts with NO yielding
either N2 and H2O (a chain terminating step) or yielding NNH and OH.
If the latter step is followed by the reactions NNH+M=N2+H+M and
H+O2=OH+O it is strongly chain branching. If, however, the subsequent
reaction is NNH+NH2=N2+NH3 or NNH+OH=N2+H2O the result is chain
termination. Consequently the NO reduction submechanism is a self
controlling explosion. Initially the chain branching sequence is
dominant and the concentration of chain carriers grows exponentially,
i.e. at a rate that is proportional to the concentration of chain
carriers. Since chain termination processes have rates that are
proportional to the square of the chain carrier concentration, they
soon limit the increase in chain carrier concentration. Thus in the
NO reduction submechanism the rate of the overall reaction rapidly
grows to a finite limit and proceeds smoothly thereafter.

        In the NO formation submechanism NH2 reacts with O, OH and
O2. The latter reaction directly produces HNO while the former two
reactions produce NH which reacts with O2 to yield HNO. The function
of HNO in the oxidation submechanism is similar to NNH, i.e.
dissocation of HNO to yield H atoms causes chain branching while
reaction with NH2 or OH causes chain termination. Thus the oxidation
submechanism, left to its own devices, would regulate the chain
carrier concentration and overall reaction rate to finite values,
though not necessarily the same values as those dicatated by the
reduction submechanism. This conflict helps make the kinetics of the
Thermal DeNOx reaction more complex than one might expect from the
number of reactions involved.

        While there is agreement between the DDHL and H&K models as
to which reactions are important, there is significant disagreement as
to the roles those reactions play. In table 1 the rate constants of
the thirty reactions the two models have in common are listed along
with the ratios of those rate constants at 1200 K. Numerically the
largest disagreement relates to the NH+O2=HNO+O reaction but this is
actually trivial since neither model assumes any reaction of NH which
could compete effectively with NH+O2=HNO+O. The disagreement as to
the rate constant for the NNH+NO=N2+HNO reaction is more important.

In the DDHL model control of the overall rate is shared between the submechanisms while the high rate constant assumed by H&K for this reaction tends to transfer control of the overall rate from the reduction submechanism to the oxidation submechanism.

Another important disagreement between the models relates to the balance between chain branching and chain termination. In the DDHL model the rate of the chain terminating reaction NH2+HNO=NH3+NO is faster by a factor of 15.8 than in the H&K model. This disagreement is compounded by the fact that in the H&K model the N2+H2O and NNH+OH channels in the NH2+NO reaction are assumed to have equal rate constants while in the DDHL model the former is 1.5 times as fast as the latter. This rate constant ratio is very critical to the kinetics since it controls the chain branching factor.

Finally it is to be noted that in the DDHL model the rate constant for the NH3+O=NH2+OH reaction is a factor of five slower than that used in the H&K model. A recent review of the literature by Cohen (17) recommends a rate constant for NH3+O=NH2+OH that is midway between the H&K and DDHL values with an uncertainty large enough to include both. The result of this and to a lesser extent the other disagreements between the models is that the concentration of O atoms during the deNOx reaction is much lower in the H&K model than it is in the DDHL model. Within DDHL NH2 is oxidized to NO chiefly by reaction with O atom but in H&K the NH2+OH=NH+H2O is more important. This leads the two models to rather different predictions of the effect of water vapor on the kinetics of the Thermal DeNOx reaction. Figures 4 and 5 show calculations of the extent of NO reductions as a function of reaction temperature done with the DDHL and H&K models. In the DDHL model adding water vapor shifts the optimum reaction to higher values, i.e. in the DDHL model added water removes O atom via the reaction O+H2O=2OH and since O is the critical chain carrier removing it with added water retards the reaction. In the H&K model, however, adding water shifts the optimum reaction temperature to lower values because the added water increases the concentration of OH, the critical chain carrier for H&K.

Since the retarding effect of water has been demonstrated experimentally (compare figures 3c and 3d, also see reference 6), this would seem to be a limitation on the H&K model. Such limitations are to be expected when an empirical model is pushed beyond the range of its data base. The DDHL model has the advantage resting on a much broader data base, one that covers all the parameters of practical importance in applications of the Thermal DeNOx process. This makes the model a useful tool in commercial application of the process, but it is to be recognized that when the model "predicts" the extent of NO reduction to be expected in a given boiler or furnace, it is merely interpolating within the base of laboratory data. When one develops a kinetic model by using the rate constants of unknown reactions as adjustable parameters, two kinds of failure are possible. The model can fail to predict kinetics for conditions outside the range of its data base because for these conditions reactions which were unimportant within the conditions of the data base become important. Such failure is less serious since it does not imply that the model is

essentially wrong, merely that it needs extension. It is also possible, however, for the adjustable parameters to produce a compensating set of errors. It is interesting to ask what experiments could be done to test the DDHL model for the latter problem.

A number of fair tests of the model are possible, i.e. in several instances the information in the model is sufficient to make unambiguous predictions about what should happen for conditions significantly different from the data base. Thus, for example, all the observations in the data base were at one atmosphere pressure and it would be interesting to see whether or not the model could correctly predict the effect of varying the pressure while holding [NH3], [NO], [H2O], and [O2] constant. Similarly the model contains the reactions known to be important during the oxidation of H2 and those which occur during CO oxidation could readily be added. Thus the model's ability to predict the extent to which adding H2 or CO shifts the optimum reaction temperature to lower values is another interesting test.

Another test of the model, one which has been carried out, involves the oxidation of NH3 at trace concentrations (19). The model's data base includes experiments in which NH3 at an initial concentration of 900 ppm was oxidized with NO initially absent. The observed decay of NH3 was zero order in NH3. This somewhat surprising behavior is a result of the balance between chain carrier production and removal. If the production of free radicals by the reaction sequence HNO+M=H+NO+M, H+O2=OH+O is balanced by their consumption by HNO+NH2=NO+NH3, it follows that [NH2] is independent of NH3 and the rate of NH3 disappearance is zero order. Obviously, however, if one starts with a sufficiently small initial concentration of NH3 this mechanism for maintaining [NH2] constant has to become ineffective and the rate of NH3 oxidation must become dependent on [NH3]. Specifically using the DDHL model one can calculate that for the conditions shown in figure 6 the decay of NH3 should be first order in NH3 and the decay constant should be 5.61/sec in contrast to the observed value of 5.65/sec. Thus in this instance, at least, the extrapolation of the DDHL model to conditions quite different from its data base is valid.

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TABLE 1

COMPARISON OF THE RATE CONSTANTS USED IN THE DDHL AND H&K
MODELS

(In this table R denotes the ratio of the DDHL rate constant to
the H&K rate constant at 1200 K.   * indicates reactions which
were found to be kinetically sensitive.)

		Reaction	A	n	E,kcal	R**
1)	DDHL	H+O2=O+OH	2.2E+14	-0.	16.80	0.97
	H&K	H+O2=O+OH	3.7E+17	-1.00	17.5	
2)	DDHL	O+H2=H+OH	1.8E+10	1.0	8.90	1.0
	H&K	O+H2=H+OH	1.8E+10	1.00	8.90	
3)	DDHL	H2+OH=H2O+H	2.2E+13	0.0	5.15	0.97
	H&K	H2+OH=H2O+H	1.17E+09	1.30	3.626	
4)	DDHL	OH+OH=O+H2O	6.3E+12	0.0	1.09	0.95
	H&K	O+H2O=OH+OH	4.60E+09	1.3	17.10	
5)	DDHL	H+O2+M=HO2+M	1.5E+E15	0.0	-0.995	1.45

(For M=H2O the quoted rate constant is increased by x21)

		Reaction	A	n	E,kcal	R**
	H&K	H+O2+M=HO2+M	7.3E+18	-1.0	0.0	

(For M = N2 or O2 the quoted A factor is changed to 6.7E+19 and
n changed to -1.42)

		Reaction	A	n	E,kcal	R**
6)	DDHL	H+HO2=OH+OH	2.5E+14	0.0	1.90	1.0
	H&K	H+HO2=OH+OH	2.5E+14	0.0	1.90	
7)	DDHL	HO2+OH=H2O+O2	5.0E+13	0.0	1.00	1.0
	H&K	HO2+OH=H2O+O2	5.0E+13	0.0	1.00	
8)	DDHL	HO2+O=O2+OH	5.0E+13	0.0	1.00	1.0
	H&K	HO2+O=O2+OH	5.0E+13	0.0	1.00	
9)	DDHL	NH3+M ◻ NH2+H+M	4.8E+16	0.00	93.90	1.83
	H&K	NH3+M ◻ NH2+H+M	2.5E+16	0.0	93.79	
10)	DDHL	NH3+H=NH2+H2	2.5E+13	0.0	17.10	1.22
	H&K	NH3+H=NH2+H2	1.3E+14	0.0	21.50	
11)	DDHL	NH3+O=NH2+OH	1.5E+12	0.0	6.04	0.23
	H&K	NH3+O=NH2+OH	2.19E+13	0.0	8.94	
12)	DDHL	NH3+OH=NH2+H2O	3.3E+12	0.0	2.12	0.71
	H&K	NH3+OH=NH2+H2O	5.75+13	0.0	8.11	
13)	DDHL	NH2+O=NH+OH*	1.7E+13	0.	1.00	0.71
	H&K	NH2+O=NH+OH	6.75E+12	0.0	0.0	

Table 1 (continued)

|					
14) DDHL	NH2+OH=NH+H2O*	5.5E+10	0.68	1.29	0.66
H&K	NH2+OH=NH+H2O	6.0E+12	0.0	0.0	
15) DDHL	NH2+H=NH+H2	5.0E+10	0.5	2.00	0.39
H&K	NH2+H=NH+H2	1.9E+13	0.0	0.0	
16) DDHL	NH2+HNO=NH3+NO*	1.8E+14	0	1.00	15.8
H&K	NH2+HNO=NH3+NO	5.0E+11	0.5	2.00	
17) DDHL	NH+O2=HNO+O	3.0E+13	0.0	3.40	110.6
H&K	NH+O2=HNO+O	1.0E+13	0.0	12.00	
18) DDHL	HNO+OH=NO+H2O	3.6E+13	0.0	0.0	0.5
H&K	HNO+OH=NO+H2O	1.26E+12	0.5	2.0	
19) DDHL	HNO+M=H+NO+M*	1.9E+16	0.0	48.68	0.4
H&K	H+NO+M=HNO+M	7.56E+15	0.0	-0.6	
20) DDHL	NO+HO2=NO2+OH	3.4E+12	0.0	-.26	1.8
H&K	NO+HO2=NO2+OH	2.09E+12	0.0	-.48	
21) DDHL	NH2+NO=NNH+OH*	6.1E+19	-2.46	1.87	0.4
H&K	NH2+NO=NNH+OH	1.26E+16	-1.25	0.0	
22) DDHL	NH2+NO=N2+H2O*	9.1E+19	-2.46	1.87	0.6
H&K	NH2+NO=N2+H2O	1.26E+16	1.25	0.0	
23) DDHL	O+NO2=NO+O2	1.0E+13	0.0	0.6	1.0
H&K	O+NO2=NO+O2	1.0E+13	0.0	0.6	
24) DDHL	NO2+H=NO+OH	3.5E+14	0.0	1.50	0.99
H&K	NO2+H=NO+OH	3.5E+14	0.0	1.48	.
25) DDHL	NO2+M=NO+O+M	1.1E16	0.0	66.00	1.6
H&K	NO+O+M=NO2+M	2.00E+15	0.0	1.88	
26) DDHL	NNH+NH2=N2+NH3*	1.0E+13	0.0	0.	1.0
H&K	NNH+NH2=N2+NH3	1.0E+13	0.0	0.0	
27) DDHL	NNH+M=N2+H+M*	2.0E+14	0.0	30.00	0.4
H&K	NNH+M=N2+H+M	2.0E+14	0.0	28.00	
28) DDHL	NNH+OH=N2+H2O	3.0E+13	0.0	0.0	1.0
H&K	NNH+OH=N2+H2O	3.0E+13	0.0	0.0	
29) DDHL	NNH+NO=N2+HNO*	9.1E+11	0.0	0.0	0.02
H&K	NNH+NO=N2+HNO	5.0E+13	0.0	0.0	
30) DDHL	NH2+O2=HNO+OH*	5.1E+13	0.0	30.00	1.4
H&K	NH2+O2=HNO+OH	4.5E+12	0.0	25.00	
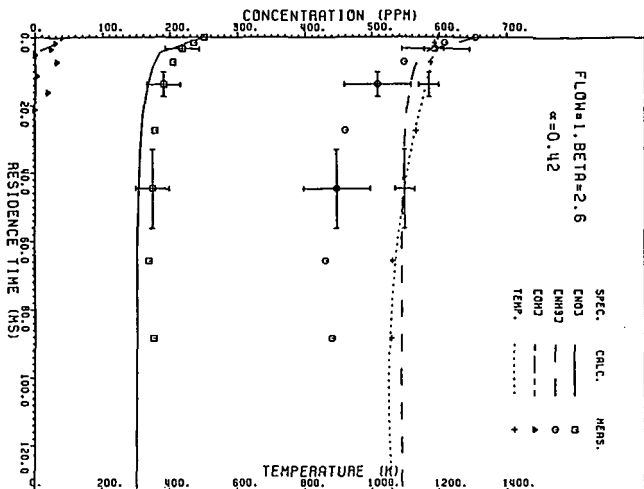
Figure 1. Comparison of H&K Model Predictions with Experiment. $NH_3/NO=2.6$

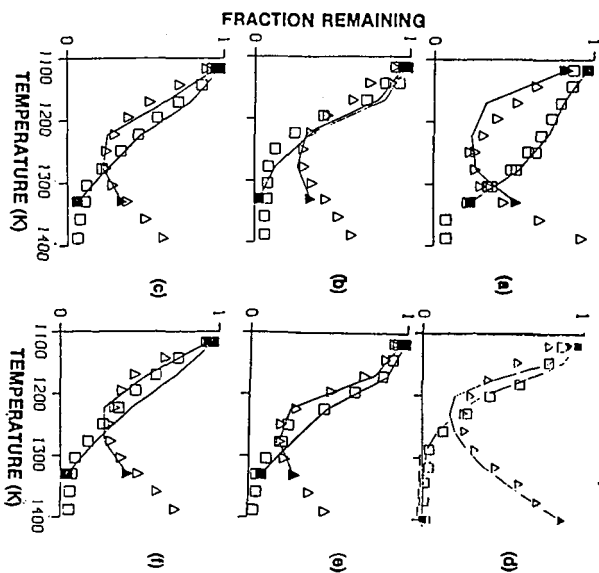**Figure 2.** Comparison of DDHL Model Predictions (Lines Terminated by ■ for NO and by ▲ for NH_3) with Experiment. □ =NO, ▲ = NH_3, t=0.1 sec, p=1.2 atm, O_2=4% (a,b,c,d), 2%(e), 8% f, NH_3=385 ppm NO=100 ppm(a), 325 ppm (b), 225 ppm (c,d, e,f), H_2O=10% (a,b,c,e,f) or 0%(c).

441

DENOx, %

NH3/NOx

Legend

△ Test Data
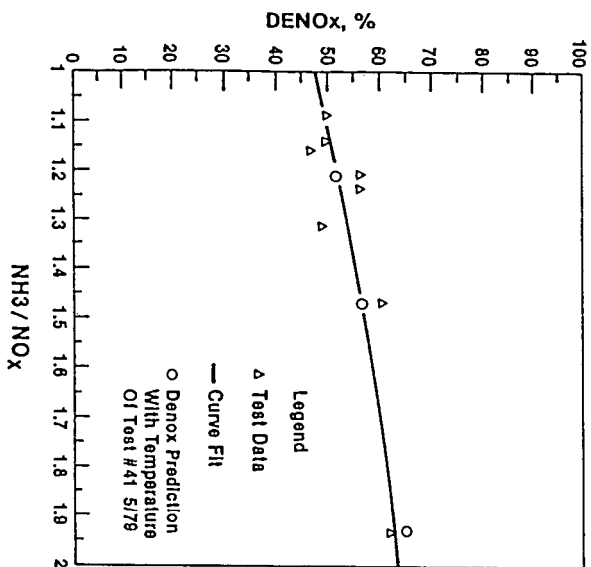
— Curve Fit

○ Denox Prediction
With Temperature
Of Test #41 5/79

Figure 3. Comparison of DDHL Model Prediction with
Observed NO Reduction in a Utility
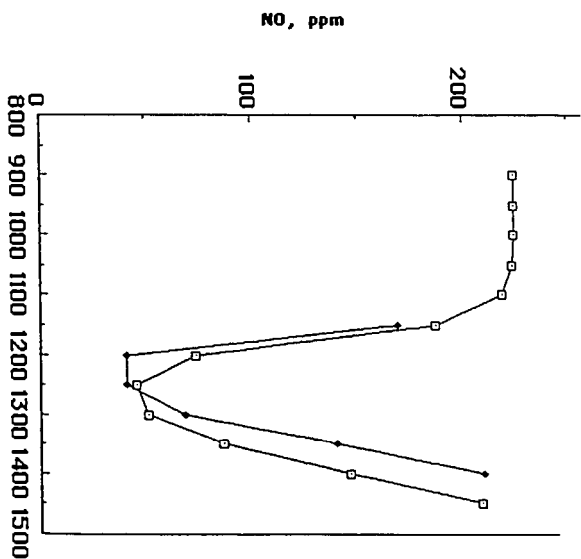Boiler, LADWP Haynes #4. Curve Fit is
to Test Data.

NO, ppm

T, K

Figure 4. Effect of H2O on DeNOx as Predicted
by DDHL Model, 4% O₂, 225 ppm NO,
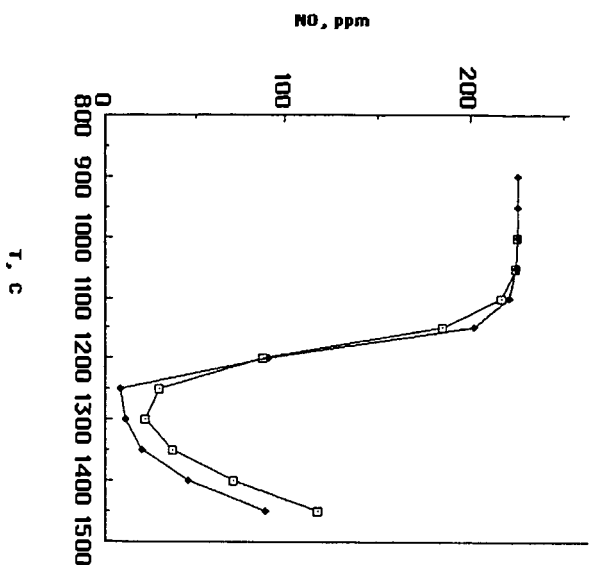385 ppm NH3, 0.1 sec reaction time
⊡=10% H₂O, ◆ = 0% H2O.

Figure 5. Effect of H₂O on DeNOx as Predicted by H&K Model, 4% O₂, 225 ppm NO, 385 ppm NH₃, 0.1 sec Reaction Time □=10% H₂O, ◆=0% H₂O.
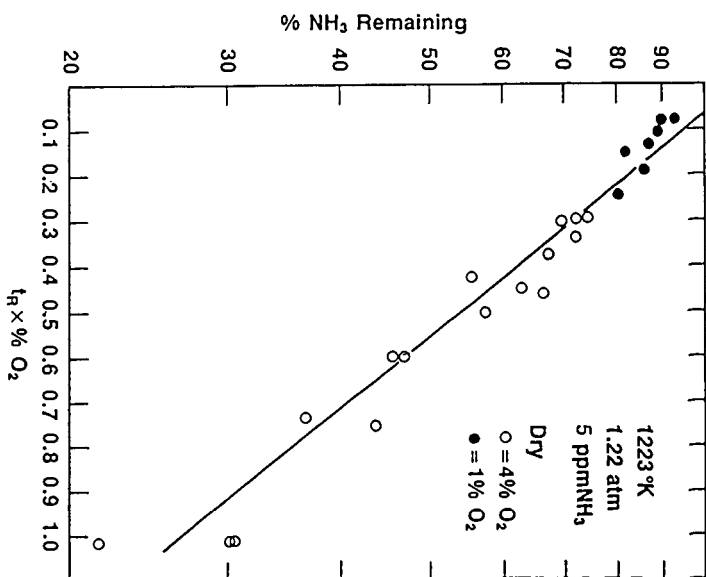
NO, ppm

T, C

Figure 6. First Order Decay of NH₃ During the Oxidation of NH₃ at Trace Concentrations

% NH₃ Remaining

1223 °K
1.22 atm
5 ppmNH₃

Dry
○ = 4% O₂
● = 1% O₂

$t_R \times \%\ O_2$

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